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RPPR Final Report
as of 09-Apr-2020

Agency Code:

Proposal Number: 62030MSPCS **Agreement Number: W911NF-14-1-0104**
INVESTIGATOR(S):

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Country: USA
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Final Report for Period Beginning 20-Jun-2014 and Ending 31-Dec-2019
Title: Engineering Ferroic and Multiferroic Materials for Active Cooling Applications
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Submitted By: Ph.D. Lane Martin Email: lwmartin@berkeley.edu
Phone: (510) 847-0254
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STEM Degrees: 2 **STEM Participants:** 2

Major Goals: The objectives of this research program are to develop a deeper understanding of the physics and thermodynamics of thermo-electrical responses in complex oxide materials with special attention to producing enhanced pyroelectric and electrocaloric effects. In particular, the program will focus on the application of such effects for advanced solid-state cooling devices. This will be achieved by implementation of a combined modeling, synthesis, characterization, and device fabrication approach and the development of a unique materials design protocol. In particular the program will work to answer the central question: what are the key materials properties that provide us with the ability to manipulate and control the temperature- and field-dependence of entropic changes required for thermo-electrical response in ferroic oxides? This will include a unique study of multiferroic materials and the development of new routes to maximize entropic changes in materials. This will enable large pyroelectric and electrocaloric responses and, in turn, enhanced cooling capacity in devices. The program will address such challenges by incorporating the PI's expertise in creating and characterizing epitaxial oxide thin-film heterostructures into a multi-faceted study of thermo-electrical properties and physics. The objectives are to expand the understanding of the fundamental mechanisms of these effects, to develop predictive capabilities for responses in real thin films, to probe the properties and ultimate performance of these materials, and to demonstrate first generation devices.
Specific Objectives and Aims
• Investigate, for the first time, the potential of coupled order parameters in multiferroics/ magnetoelectrics to enhance thermo-electrical responses via so-called magneto-electro-caloric and pyro-electric-magnetic effects.
• Utilize epitaxial thin-film synthesis techniques to exerting control over phase transformations, ferroic domain structures, and interfaces in multiferroic and novel frustrated ferroelectric heterostructures that will enable enhanced thermo-electrical responses.
• Expand phenomenological models of these thermodynamic properties beyond 1D approaches to include polydomain structures, multi-layered heterostructures, compositional and strain gradients, and other features common in real films.
• Overcome inadequacies in characterization of such properties through the development of new techniques to provide direct measurement of temperature changes.
• Demonstrate rudimentary solid-state refrigeration devices based on ferroic and multiferroic materials – including work towards cooling to 70K and below.

Accomplishments: During the 6 month no-cost extension (NCE), a number of important accomplishments were completed including publication of 11 peer-review papers including papers in Advanced Materials (1), Nano Letters (1), Nature Communications (2), Advanced Functional Materials (1), and others. The major accomplishments can be summarized as follows

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1) Advances in the study of electro-thermal effects in ferroic thin films – We continued our contributions in this space, including we directly measuring the magnitude and sign of the intrinsic, extrinsic, dielectric, and secondary pyroelectric contributions to the total pyroelectric response as a function of chemistry in thin films of PbZr1−xTixO3 (x = 0.40, 0.48, 0.60, and 0.80) using phase-sensitive frequency and applied dc-bias methods [ACS Appl. Mater. Inter. 11, 35146 (2019)]. Additionally, we measured the nature of pyroelectric response in thin films of the multiferroic Bi1−xLaxFeO3 (x = 0–0.45) wherein lanthanum substitution results in a chemically induced lowering of the ferroelectric-to-paraelectric and structural-phase transition and a 100% increase in the room temperature pyroelectric response [APL Mater. 7, 111111 (2019)].
2) High-performance materials: Relaxor ferroelectrics – We also developed novel understanding in complex relaxor materials including probing the effect of intrinsic point defects on relaxor properties of 0.68PbMg1/3Nb2/3O3-0.32 PbTiO3 thin films via ex post facto ion bombardment. Increasing defect concentration was found to weaken relaxor character because of the strong interactions between defect dipoles and the polarization [Phys. Rev. Lett. 123, 207602 (2019)]. Also, we studied finite-size effects on relaxor order in 7-70-nm-thick films of PbSc0.5Ta0.5O3 wherein below ~ 30 nm, suppression of relaxor order rapidly accelerates corresponding to the polarization correlations lengths being approximately the same as the film thickness [Phys. Rev. B 101, 094102 (2020), Editor's Suggestion].
3) Emergent function from novel approaches – We showed the ability to produce large ferroelectric polarization and dielectric permittivity (PbZr0.8Ti0.2O3)n/(PbZr0.4Ti0.6O3)2n superlattices. In intermediate-period (n = 4) superlattices we found evidence of layers acting like both the parents and the MPB composition – giving rise to the novel properties [Adv. Electron. Mater. 1901395 (2020)]. We also leveraged machine-learning approaches like deep sequence-to-sequence autoencoders to automate the extraction of latent features of nanoscale ferroelectric switching from piezoresponse force spectroscopy. We classified and quantified nanoscale-switching mechanisms and identified elastic hardening events which are associated with the nucleation and growth of charged domain walls [Nature Commun. 10, 4809 (2019)].

Over the duration of the full program, we produced 70 publications (13, 10, 12, 12, 12, and 11 in Years 1, 2, 3, 4, 5, and the NCE, respectively) as of the writing of this report. This includes articles in Nature (1), Nature Materials (4), Advanced Materials (10), Nature Communications (7), ACS Nano (3), Nano Letters (3), Physical Review Letters (1), Advanced Functional Materials (2), and many others. The major contributions of this work over the years include, but are not limited to, impacts in:
1) Advances in the study of electro-thermal effects in ferroic thin films – From the development of novel ways to measure both pyroelectric and electrocaloric responses in thin-film materials with higher precision than ever done before to demonstrating record-breaking pyroelectric energy conversion from low-grade thermal sources we have leveraged our fundamental contributions in measurement science to make impact in our ability to produce and control materials in thoughtful ways. In turn, we have provided the most indepth studies of such properties in a range of materials. These included classical ferroelectrics, like PbZr0.2Ti0.8O3 where we have quantified the "extrinsic" contributions to pyroelectricity due to changes between the ferroelastic domain population among other effects. We have also completed direct electrocaloric measurements for the first time and highlighted that pyroelectric and electrocaloric effects are enhanced due to the exact-opposite effects from the extrinsic contributions under tensile strain. We have also probed non-classical materials like silicon-doped HfO2 and proven that it is indeed polar and ferroelectric, has pyroelectric response, and that the electrocaloric response is larger than expected due to defects which can contribute to configurational or dipolar entropy. This program enable the PI to be a world leader in this space.
2) Rewriting the role of domains/domain walls in material function – From day one, we have provided fundamental know-how as to the role of domain walls in the response of ferroelectric materials. This includes demonstrating novel domain-wall-based effects that can contribute to large dielectric response, developing new orientation-dependent phenomenological models to probe domain structures and properties in ferroelectrics, identifying new pathways to ferroelectric switching in (111)-oriented ferroelectrics, used compositional gradients in films to tune the energy landscape for ferroelectric domains such that novel function – including spring-like responses and large electromechanical effects, and even shown that domain walls, which have long been thought to be a hindrance because they lead to high dielectric loss and hysteresis in the device response to an applied electric field, can be used for good in creating high-performance and tunable microwave dielectrics.
3) Design and understanding of emergent polarization physics – A theme of our work has been the identification of routes to produce exotic, unexpected, and greatly enhanced stimuli-induced effects in ferroic materials. We have produced complex topologies of electrical polarization - namely, nanometer-scale vortex arrays that are reminiscent of rotational spin topologies - by making use of the competition between charge, orbital, and lattice degrees of freedom in superlattices of alternating PbTiO3 and SrTiO3. In turn, we showed that these vortices can coexist with classical ferroelectric domain structures and that they interconversion is mediated by a first-order phase transition.

At room temperature, the coexisting vortex and ferroelectric phases form a mesoscale, fiber-textured hierarchical superstructure and the vortex phase possesses an axial polarization, set by the net polarization of the surrounding ferroelectric domains, such that it possesses a multi-order-parameter state and belongs to a class of gyrotropic electrotoroidal compounds. Application of electric fields permits interconversion between the vortex and the ferroelectric phases concomitant with order-of-magnitude changes in piezoelectric and nonlinear optical responses. Finally, using novel growth approaches, such as compositional gradients, we produced large spatial gradients in ferroelectric polarization (changes of 35 μC/cm2 across a 150 nm thick film). This gave rise to large dielectric permittivity with low loss ($\varepsilon r = 775$, $\tan \delta < 0.05$), negligible temperature-dependence (13% deviation over 500°C) and high-dielectric tunability (greater than 70% across a 300°C range).
4) Developing precise control and understanding of ferroic materials: Chemistry and defect control – We have regularly used defects and chemistry to effect deterministic change on materials. For example, we used defect dipoles to expand the lattice and increase the transition temperature of $BaTiO_3$, have tweaked chemistry in materials like $BiFeO_3$ and others to tune properties, have used ion beams to effect changes in defect structures in materials like $PbTiO_3$, $BiFeO_3$, and others, induced ferroelectric order in antiferroelectric using cation chemistry, and even tuned local switching behavior in materials by tuning defect structures using a He-ion microscope.

Training Opportunities: The training and professional development activities presented as part of this project include:
1) For the graduate students and postdocs working on the program, extensive one-on-one work with the PI has occurred. In the Martin group, the researchers working on this ARO-supported program took part in weekly sub-group meetings (including the PI) working on related materials and problems. At these meetings the researchers presented their work, discussed challenges and prospects for their research program, and generally interacted at a high level. Additional individual meetings were scheduled to address specific research results and work. The PI works closely with the students on the paper writing process as well – including hands-on, one-on-one sessions working through the text of the papers. The formal meetings were augmented by frequent visits by the PI and discussions of ongoing research in the laboratory on a day-to-day basis.
2) For the undergraduate students working on this program in the Martin group, there were formal weekly meetings (plus informal shadowing and interactions) with the program supported graduate student mentor. In addition to this, the undergraduate student was a participant in the weekly sub-team meetings, and had monthly meetings with the PI and the graduate student mentor to assess progress, understanding of topics, and near- and long-term research and education goals.
3) All graduate students and postdocs supported by this program were participants in regular seminar/presentation training.
4) These experiences were further augmented by weekly group meeting presentations hosted by the PI. The PI supervises a graduate student organized formal research symposium for their group members at which the weekly presenter gives a lengthy and detailed presentation and is subject to ample questions advice. This is one of the most well-received professional development activities and really forces students to up their game.
5) The graduate students and postdocs supported on this program gave oral and poster presentations on their research at various national meetings, including different MRS, EMA, APS, etc. meetings.
6) The graduate students and postdocs supported by this program have participated in the writing of successful user proposals to the CNMS at Oak Ridge National Laboratory and APS at Argonne National Laboratory and have spent multiple batches of time at both institution completing program-related work.

Results Dissemination: The results of this work have been disseminated to the communities of interest in multiple ways:
1) The supported students, postdocs, and PI have generated publications – 70 of which have been published during the duration of this work – which have and, will continue, to be disseminated in high-impact, peer-reviewed journals that are read by the community.
2) The students, postdocs, and PI are presenting presentations and posters at national conferences and workshops attended by members of the research community. This includes invited talks for the PI at meetings around the world.
3) The PI participates in considerable outreach to prospective undergraduate scientists and engineers and includes in presentations and demonstrations presented to this students aspects of research that are derived from this program. These sessions often include family members (parents, siblings) and thus the message reaches a wide-range of people. PI Martin has also spoken, on the record, at numerous public panels aimed at educating the general public about the needs for and importance of sustained, long-term support of basic research initiatives.
4) PI Martin is actively participating as a scientific adviser for a start-up company and is applying the know-how derived in part from this ARO-supported program to the development of new high-tech industries in the United States.

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Honors and Awards: 1. 2018, 2019 Highly Cited Researcher – Ranked in the top 1% by citations for field and publication year in Web of Science (Nov. 2018, 2019)
2. 2019 Zeiss ORION NanoFab Prize, Carl Zeiss SMT, Inc. (for innovative work on using ion beams to control material properties and the demonstration of the value of the NanoFab) (Oct. 2019).
3. IEEE-Ultrasonics, Ferroelectrics, and Frequency Control (UFFC) Society Ferroelectrics Young Investigator Award (July 2019)
4. Defense Science Study Group (DSSG) 2020-2021, Institute for Defense Analyses (IDA) and Defense Advanced Research Projects Agency (DARPA) (Mar. 2019)
5. 2017 Excellence in Laboratory Safety Grand Prize, UC Berkeley Environmental, Health, and Safety (EHS) (Feb. 2018)
6. Robert L. Coble Award for Young Scholars, American Ceramic Society (Oct. 2016)
7. American Association for Crystal Growth (AACG) Young Author Award (Aug. 2015)

Protocol Activity Status:

Technology Transfer: The team continues interactions to support technology transfer, including:
1) Increased and Sustained Interactions with the Army Research Laboratory (Adelphi, MD) – Building from a number of years of continued interactions with Dr. Ron Polcawich and Dr. Brendan Hanrahan at ARL, strong relationships are now being formalized with Cooperative Agreements and co-funding opportunities. PI Martin has visited Dr. Ron Polcawich (now on rotation at DARPA), Dr. Brendan Hanrahan, Mr. Jeff Pulskamp, Dr. Ryan Rudy, Dr. William Nothwang, and others, to lay the foundation for the Cooperative Agreement – a small version of which is now in place. Based on the efforts of PI Martin and others, there are numerous funding avenues for joint efforts to explore the translation and scaling of materials systems developed by PI Martin to ARL efforts. In particular, efforts in high-frequency/microwave dielectrics, advanced actuator, and pyroelectric energy conversion – leveraging the efforts and materials developed in this ARO program – are planned. Materials are being exchanged. This work is a highly complimentary application to the core programmatic goals of this ARO program.
2) Interactions with Neothermal Energy Company (Atlanta, GA) - Continued interactions as a Scientific Advisor for this small start-up company working on the commericalization of pyroelectric energy conversion for waste-heat energy conversion. Commensurate with the work with ARL, this work is highly complimentary application to the core programmatic goals of this ARO program.

PARTICIPANTS:

Participant Type: PD/PI
Participant: Lane W. Martin
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Pravin Kavle
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Yizhe Jiang
Person Months Worked: 5.00 **Funding Support:**
Project Contribution:

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International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

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Publication Identifier Type: DOI Publication Identifier: 10.1002/adma.201400254
Volume: 2.6E+001 Issue: 3.6E+001 First Page #: 6341
Date Submitted: Date Published:
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Article Title: Enhancement of Ferroelectric Curie Temperature in BaTiO
Authors:
Keywords: ferroelectric, BaTiO3, enhanced Tc, thin films
Abstract: In this work, we highlight how, when combined with thin-fi lm epitaxy, the presence of such defect dipoles can give rise to enhanced ferroelectric ordering in materials and can explain many of the effects in BaTiO3 noted above. By directly coupling the electrical and elastic dipoles of the defect complexes with the polarization and epitaxial strain state of the fi lm, respectively, we can align the defects thereby inducing an additional anisotropic lattice deformation. Such a coupling of the elastic dipole of the defects with stress has been demonstrated before, but here we develop a new paradigm in strain control of ferroelectric materials whereby we leverage this and the corresponding coupling with the primary order parameter of the material to enhance performance. We demonstrate that in BaTiO3 films, known to possess a strong coupling between strain and polarization, that deterministically controlling the electric- and elastic-dipole moments of engineered defect complexes allows us
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Volume: 1.16E+002 Issue: 1.9E+001 First Page #: 194509
Date Submitted: Date Published:
Publication Location:
Article Title: High-frequency thermal-electrical cycles for pyroelectric energy conversion
Authors:
Keywords: pyroelectric, thin films, energy conversion, BaTiO3
Abstract: We report thermal to electrical energy conversion from a 150nm thick BaTiO3 film using pyroelectric cycles at 1 kHz. A microfabricated platform enables temperature and electric field control with temporal resolution near 1 ls. The rapid electric field changes as high as 11┐x10^5kV/cm-s, and temperature change rates as high as 6┐x10^5K/s allow exploration of pyroelectric cycles in a previously unexplored operating regime. We investigated the effect of phase difference between electric field and temperature cycles, and electric field and temperature change rates on the electrical energy generated from thermal-electrical cycles based on the pyroelectric Ericsson cycle. Complete thermodynamic cycles are possible up to the highest cycle rates tested here, and the energy density varies significantly with phase shifts between temperature and electric field waveforms. This work could facilitate the design and operation of pyroelectric cycles at high cycle rates, and aid in the design of new py
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Date Submitted: Date Published:
Publication Location:
Article Title: Enhanced electrocaloric and pyroelectric response from ferroelectric multilayers
Authors:
Keywords: electrocaloric, pyroelectric, ferroelectric, multilayers
Abstract: Room temperature pyroelectric properties and adiabatic temperature change of (001)-textured ferroelectric multilayers on Si are computed by taking into account electrostatic interlayer interactions and thermal strains. We show that by adjusting internal electrical fields through changing relative thicknesses in a multilayer ferroelectric construct, electrothermal properties can be significantly enhanced. A quantitative analysis is provided for BaTiO3-PbZr0.2Ti0.8O3 (BTO-PZT) and SrTiO3-PbZr0.2Ti0.8O3 (STO-PZT) multilayers. For instance, 0.74 ˪ BTO-0.26 ˪PZT and 0.35 ˪STO-0.65 ˪PZT bilayers show ˩ 120% and 65% increase in electrocaloric response, respectively, compared to PZT films on Si for delta-E = 500 kV/cm.
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Date Submitted: Date Published:
Publication Location:
Article Title: Reduction of the electrocaloric entropy change of ferroelectric
Authors:
Keywords: electrocaloric, PbZr1-xTixO3, thin films, elastocaloric
Abstract: We report laser-based direct measurements of the pyroelectric and electrocaloric effects of PbZr1?xTixO3 epitaxial layers as a function of temperature and electric field. By evaluating the differences between the total pyroelectric and electrocaloric coefficients, we determine the secondary contribution to the electrocaloric effect that is created by a combination of piezoelectric and elastocaloric effects. The secondary contribution to the electrocaloric coefficient has the opposite sign as the primary effect and therefore reduces the overall entropy change of PbZr1?xTixO3 in an electric field. The absolute magnitude of the secondary effect is comparable to the primary effect at elevated temperatures of ˧ 200 °C.
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Publication Identifier Type: DOI Publication Identifier: 10.1021/am506436s
Volume: 6.0E+000 Issue: 2.4E+001 First Page #: 22436
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Publication Location:
Article Title: Effects of Nonequilibrium Growth, Nonstoichiometry, and Film Orientation on the Metal-to-Insulator Transition in NdNiO
Authors:
Keywords: thin films, NdNiO3, metal-to-insulator transition, chemical effects
Abstract: Next-generation devices will rely on exotic functional properties not found in traditional systems. One class of materials of particular interest for applications are those possessing metal-to-insulator transitions (MITs). In this work, we probe the relationship between variations in the growth process, subsequent variations in cation stoichiometry, and the MIT in NdNiO3 thin films. Slight variations in the growth conditions, in particular the laser fluence, during pulsed-laser deposition growth of NdNiO3 produces films that are both single-phase and coherently strained to a range of substrates despite possessing as much as 15% Nd-excess. Subsequent study of the temperature-dependence of the electronic transport reveals dramatic changes in both the onset and magnitude of the resistivity change at the MIT with increasing cation nonstoichiometry giving rise to a decrease (and ultimately a suppression) of the transition and the magnitude of the resistivity change. From there, the electron
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Volume: 6.0E+000 Issue: 0 First Page #: 6136
Date Submitted: Date Published:
Publication Location:
Article Title: Ferroelectrically driven spatial carrier density modulation in graphene
Authors:
Keywords: LiNbO3, graphene, ferroelectric, devices
Abstract: The next technological leap forward will be enabled by new materials and inventive means of manipulating them. Among the array of candidate materials, graphene has garnered much attention; however, due to the absence of a semiconducting gap, the realization of graphene-based devices often requires complex processing and design. Spatially controlled local potentials, for example, achieved through lithographically defined split-gate configurations, present a possible route to take advantage of this exciting two-dimensional material. Here we demonstrate carrier density modulation in graphene through coupling to an adjacent ferroelectric polarization to create spatially defined potential steps at 180¬-domain walls rather than fabrication of local gate electrodes. Periodic arrays of p–i junctions are demonstrated in air (gate tunable to p–n junctions) and density functional theory reveals that the origin of the potential steps is a complex interplay between polarization, chemistry, and defe
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Volume: 9.1E+001 Issue: 6.0E+000 First Page #: 64413
Date Submitted: Date Published:
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Article Title: Magnetically disordered phase in epitaxial iron-deficient
Authors:
Keywords: Fe3O4, thin films, magnetic, defect structures, new phase
Abstract: We report on the transport and magnetic properties of iron-deficient Fe3O4 (Fe3??O4) thin films grown with pulsed-laser deposition, where the stoichiometry and amount of cation vacancies are precisely controlled through changes in the oxygen partial pressure during growth. As the stoichiometry evolves from Fe3O4 to ? -Fe2O3, three distinct structural and magnetic regimes emerge: a Fe3O4-like regime, a ? -Fe2O3-like regime, and a transition regime. While reflection high-energy electron diffraction measurements reveal that films in all three regimes grow epitaxially cube-on-cube on MgO substrates, the transition-regime films are characterized by an absence of long-range, out-of-plane ordering in the film. Selected area electron diffraction measurements reveal the transition-regime films are well ordered on a local level, but not throughout the entire film. The structural disorder of the transition-regime films does not manifest itself in the transport properties, where a systematic chang
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Volume: 2.7E+001 Issue: 5.0E+000 First Page #: 861
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Article Title: A Novel, Layered Phase in Ti-Rich SrTiO
Authors:
Keywords: novel phase, Sr2Ti7O14, layered structure, thermal glass
Abstract: Here, we study the growth, structure, and properties of the Ti-rich portion of the SrTiO3 –TiO 2 phase diagram in and around the eutectic composition. We observe that the non-equilibrium nature of the growth process results in fi lms that greatly exceed the thermodynamic solubility limit of Ti in SrTiO3 (?0.5 mol% of Ti in bulk SrTiO3 as compared with ?130 mol% of Ti in SrTiO3 in the current study) and the eventual formation of a layered, Ti-rich phase with nominal chemical formula Sr2Ti7O14 . Scanning transmission electron microscopy (STEM)-based studies map out the structure and valence state of this phase, first-principles approaches explore the phase stability and electronic properties, and studies of the dielectric, optical, thermal, and magnetic properties reveal diminished dielectric permittivity (and low dielectric loss), an enhanced bandgap, glass-like thermal conductivity, and the potential for 2D anti-ferromagnetism.
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Article Title: Polarization screening-induced magnetic phase gradients at complex oxide interfaces
Authors:
Keywords: multiferroic, magnetoelectric, interfacial coupling, interfacial reconstruction
Abstract: Thin-film oxide heterostructures show great potential for use in spintronic memories, where electronic charge and spin are coupled to transport information. Here we use a La0.7Sr0.3MnO3 (LSMO)/PbZr0.2Ti0.8O3 (PZT) model system to explore how local variations in electronic and magnetic phases mediate this coupling. We present direct, local measurements of valence, ferroelectric polarization and magnetization, from which we map the phases at the LSMO/PZT interface. We combine these experimental results with electronic structure calculations to elucidate the microscopic interactions governing the interfacial response of this system. We observe a magnetic asymmetry at the LSMO/PZT interface that depends on the local PZT polarization and gives rise to gradients in local magnetic moments; this is associated with a metal–insulator transition at the interface, which results in significantly different charge-transfer screening lengths. This study establishes a framework to understand the fundam
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Volume: 9.1E+001 Issue: 1.4E+001 First Page #: 144106
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Article Title: Orientation-dependent structural phase diagrams and dielectric properties of
Authors:
Keywords: GLD models, PbZr1-xTixO3, thin films, epitaxy, polydomain, orientations
Abstract: The orientation-dependent equilibrium ferroelectric domain structures and dielectric properties of polydomain PbZr1?xTixO3 thin films are investigated using a phenomenological Ginzburg-Landau-Devonshire thermodynamic model. We develop and describe three-dimensional polydomain models for (001)-, (101)-, and (111)-oriented films and explore the evolution of the structure and dielectric permittivity of the system as a function of epitaxial strain across the composition range 0.5 ┐< x <┐ 1.0. Our studies reveal that the film orientation, epitaxial strain, and composition can combine in unexpected ways to drive exotic phase stability and transformations which have intriguing implications for the properties. In particular, in (101)- and (111)-oriented films, the application of epitaxial strains along non-┐001└-type crystallographic directions significantly reduces the stability range of the parent tetragonal phase [which is dominant in (001)-oriented films] and results in a variety of new sy
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Article Title: Epitaxial growth of highly-crystalline spinel ferrite thin films on perovskite substrates for all-oxide devices
Authors:
Keywords: magnetoelectric, multiferroic, spinel, thin films, devices, film growth
Abstract: The potential growth modes for epitaxial growth of Fe3O4 on SrTiO3 (001) are investigated through control of the energetics of the pulsed-laser deposition growth process (via substrate temperature and laser fluence). We find that Fe3O4 grows epitaxially in three distinct growth modes: 2D-like, island, and 3D-to-2D, the last of which is characterized by films that begin growth in an island growth mode before progressing to a 2D growth mode. Films grown in the 2D-like and 3D-to-2D growth modes are atomically flat and partially strained, while films grown in the island growth mode are terminated in islands and fully relaxed. We find that the optimal structural, transport, and magnetic properties are obtained for films grown on the 2D-like/3D-to-2D growth regime boundary. The viability for including such thin films in perovskite-based all-oxide devices is demonstrated by growing a Fe3O4/La0.7Sr0.3MnO3 spin valve epitaxially on SrTiO3.
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Article Title: Complex Evolution of Built-in Potential in Compositionally-Graded PbZr1-xTixO3 Thin Films
Authors:
Keywords: PbZr1-xTixO3, compositionally-graded thin films, dielectric, ferroelectric, flexoelectric
Abstract: Epitaxial strain has been widely used to tune crystal and domain structures in ferroelectric thin films. New avenues of strain engineering based on varying the composition at the nanometer scale have been shown to generate symmetry breaking and large strain gradients culminating in large built-in potentials. In this work, we develop routes to deterministically control these built-in potentials by exploiting the interplay between strain gradients, strain accommodation, and domain formation in compositionally graded PbZr1 ┌xTixO3 heterostructures. We demonstrate that variations in the nature of the compositional gradient and heterostructure thickness can be used to control both the crystal and domain structures and give rise to nonintuitive evolution of the built-in potential, which does not scale directly with the magnitude of the strain gradient as would be expected. Instead, large built-in potentials are observed in compositionally-graded heterostructures that contain (1) compositional
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Article Title: Ferroelectric polarization reversal via successive ferroelastic transitions
Authors:
Keywords: ferroelectric, PbZr1-xTixO3, (111), switching
Abstract: Switchable polarization makes ferroelectrics a critical component in memories, actuators and electro-optic devices, and potential candidates for nanoelectronics. Although many studies of ferroelectric switching have been undertaken, much remains to be understood about switching in complex domain structures and in devices. In this work, a combination of thinfilm epitaxy, macro- and nanoscale property and switching characterization, and molecular dynamics simulations are used to elucidate the nature of switching in PbZr0.2Ti0.8O3 thin films. Di← erences are demonstrated between (001)-/(101)- and (111)-oriented films, with the latter exhibiting complex, nanotwinned ferroelectric domain structures with high densities of 90♬ domain walls and considerably broadened switching characteristics. Molecular dynamics simulations predict both 180 degree♬ (for (001)-/(101)-oriented films) and 90 degree♬ multi-step switching (for (111)-oriented films) and these processes are subsequently observed in st
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Date Submitted: 7/27/16 12:00AM Date Published: 10/1/15 7:00AM
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Article Title: 180° Ferroelectric Stripe Nanodomains in BiFeO
Authors: Zuhuang Chen, Jian Liu, Yajun Qi, Deyang Chen, Shang-Lin Hsu, Anoop R. Damodaran, Xiaoqing He, A
Keywords: BiFeO3, domain walls, exchange bias, ferroelectric, multiferroic, strain
Abstract: There is growing evidence that domain walls in ferroics can possess emergent properties that are absent in the bulk. For example, 180° ferroelectric domain walls in the ferroelectric-antiferromagnetic BiFeO3 are particularly interesting because they have been predicted to possess a range of intriguing behaviors, including electronic conduction and enhanced magnetization. To date, however, ordered arrays of such domain structures have not been reported. Here, we report the observation of 180° stripe nanodomains in (110)-oriented BiFeO3 thin films grown on orthorhombic GdScO3 (010)O substrates and their impact on exchange coupling to metallic ferromagnets. Nanoscale ferroelectric 180° stripe domains with {112?} domain walls were observed in films <32 nm thick. With increasing film thickness, we observed a domain structure crossover from the depolarization field-driven 180° stripe nanodomains to 71° ferroelastic domains determined by the elastic energy. These 180° domain walls (which...
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Article Title: Ultrafast Terahertz Gating of the Polarization and Giant Nonlinear Optical Response in BiFeO
Authors: Frank Chen, John Goodfellow, Shi Liu, Ilya Grinberg, Matthias C. Hoffmann, Anoop R. Damodaran, Yi Z
Keywords: BiFeO3, terahertz, modulation of polarization, optical
Abstract: Here, we use THz pulses as an all-optical bias to apply sub-picosecond duration electric fields to BiFeO3 (BFO) thin films. We show that these generate large amplitude changes in the ferroelectric polarization and the associated nonlinear optical properties. Observed modulations in the intensity of the second harmonic light generated by the thin film correspond to on–off ratios of 220× gateable on few hundred femtosecond timescales. These effects are enhanced through the use of rare earth doping to position the sample at a morphotropic phase boundary where the electromechanical and nonlinear optical responses are magnified but where the dynamical response of these materials has not previously been explored. Additionally, metallic electrode structures are used to both electrically bias and to further enhance the applied THz fields through subdiffraction limit focusing within a nanogap. These results open up possibilities for wideband, high contrast THz-frequency...
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Article Title: Structural phase diagram and pyroelectric properties of free-standing ferroelectric/non-ferroelectric multilayer heterostructures
Authors: Jialan Zhang, Josh C. Agar, Lane W. Martin
Keywords: modeling, ferroelectric, pyroelectric, free-standing heterostructures
Abstract: Ginzburg-Landau-Devonshire models are used to explore ferroelectric phases and pyroelectric coefficients of symmetric free-standing, thin-filmtrilayerheterostructures composed of a ferroelectric and two identical non-ferroelectric layers. Using BaTiO3 as a model ferroelectric, we explore the influence of temperature, in-plane misfit strain, and the non-ferroelectric layer (including effects of elastic compliance and volume fraction) on the phase evolution in the ferroelectric. The resulting phase diagram reveals six stable phases, two of which are not observed for thin films on semi-infinite cubic substrates. From there, we focus on heterostructures with non-ferroelectric layers of commonly available scandate materials which are widely used as substrates for epitaxial growth. Again, six phases with volatile phase boundaries are found in the phase diagram for the NdScO3/BaTiO3/NdScO3 trilayerheterostructures. The evolution of polarization and pyroelectric coefficients in the free-...
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Article Title: Observation of polar vortices in oxide superlattices
Authors: A. K. Yadav, C. T. Nelson, S. L. Hsu, Z. Hong, J. D. Clarkson, C. M. Schlepütz, A. R. Damodaran, P. S
Keywords: ferroelectric, superlattice, vortex, emergenet state
Abstract: The complex interplay of spin, charge, orbital and lattice degrees of freedom provides a plethora of exotic phases and physical phenomena1, 2, 3, 4, 5. In recent years, complex spin topologies have emerged as a consequence of the electronic band structure and the interplay between spin and spin–orbit coupling in materials6, 7. Here we produce complex topologies of electrical polarization—namely, nanometre-scale vortex–antivortex (that is, clockwise–anticlockwise) arrays that are reminiscent of rotational spin topologies6—by making use of the competition between charge, orbital and lattice degrees of freedom in superlattices of alternating lead titanate and strontium titanate layers. Atomic-scale mapping of the polar atomic displacements by scanning transmission electron microscopy reveals the presence of long-range ordered vortex–antivortex arrays that exhibit nearly continuous polarization rotation. Phase-field modelling confirms that the vortex array is the low-energy state for a...
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Publication Location:
Article Title: Asymmetric Response of Ferroelastic Domain-Wall Motion under Applied Bias
Authors: Michael L. Jablonski, Shi Liu, Christopher R. Winkler, Anoop R. Damodaran, Ilya Grinberg, Lane W. Mar
Keywords: bismuth ferrite, domain switching, ferroelastic, in situ, multiferroic
Abstract: The switching of domains in ferroelectric and multiferroic materials plays a central role in their application to next-generation computer systems, sensing applications, and memory storage. A detailed understanding of the response to electric fields and the switching behavior in the presence of complex domain structures and extrinsic effects (e.g., defects and dislocations) is crucial for the design of improved ferroelectrics. In this work, in situ transmission electron microscopy is coupled with atomistic molecular dynamics simulations to explore the response of 71° ferroelastic domain walls in $BiFeO_3$ with various orientations under applied electric-field excitation. We observe that 71° domain walls can have intrinsically asymmetric responses to opposing biases. In particular, when the electric field has a component normal to the domain wall, forward and backward domain-wall velocities can be dramatically different for equal and opposite fields. Additionally, the presence of defects..
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Article Title: Highly mobile ferroelastic domain walls in compositionally graded ferroelectric thin films
Authors: J. C. Agar, A. R. Damodaran, M. B. Okatan, J. Kacher, C. Gammer, R. K. Vasudevan, S. Pandya, L. R.
Keywords: ferroelectric, domain wall, thin film, device
Abstract: Domains and domain walls are critical in determining the response of ferroelectrics, and the ability to controllably create, annihilate, or move domains is essential to enable a range of next-generation devices. Whereas electric-field control has been demonstrated for ferroelectric 180° domain walls, similar control of ferroelastic domains has not been achieved. Here, using controlled composition and strain gradients, we demonstrate deterministic control of ferroelastic domains that are rendered highly mobile in a controlled and reversible manner. Through a combination of thin-film growth, transmission-electron-microscopy-based nanobeam diffraction and nanoscale band-excitation switching spectroscopy, we show that strain gradients in compositionally graded PbZr1?xTixO3 heterostructures stabilize needle-like ferroelastic domains that terminate inside the film. These needle-like domains are highly labile in the out-of-plane direction under applied electric fields, producing a locally...
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Date Submitted: 7/27/16 12:00AM Date Published: 7/1/16 7:00AM
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Article Title: New modalities of strain-control of ferroelectric thin films
Authors: Anoop R Damodaran, Joshua C Agar, Shishir Pandya, Zuhuang Chen, Liv Dedon, Ruijuan Xu, Brent Ap
Keywords: ferroelectric, thin films, epitaxy, strain
Abstract: Ferroelectrics, with their spontaneous switchable electric polarization and strong coupling between their electrical, mechanical, thermal, and optical responses, provide functionalities crucial for a diverse range of applications. Over the past decade, there has been significant progress in epitaxial strain engineering of oxide ferroelectric thin films to control and enhance the nature of ferroelectric order, alter ferroelectric susceptibilities, and to create new modes of response which can be harnessed for various applications. This review aims to cover some of the most important discoveries in strain engineering over the past decade and highlight some of the new and emerging approaches for strain control of ferroelectrics. We discuss how these new approaches to strain engineering provide promising routes to control and decouple ferroelectric susceptibilities and create new modes of response not possible in the confines of conventional strain engineering. To conclude, we will...
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Article Title: Single gate p-n junctions in graphene-ferroelectric devices
Authors: J. Henry Hinnefeld, Ruijuan Xu, Steven Rogers, Shishir Pandya, Moonsub Shim, Lane W. Martin, Nadya
Keywords: ferroelectric, graphene, junctions, devices
Abstract: Graphene's linear dispersion relation and the attendant implications for bipolar electronics applications have motivated a range of experimental efforts aimed at producing p-n junctions in graphene. Here we report electrical transport measurements of graphene p-n junctions formed via simple modifications to a PbZr0.2Ti0.8O3 substrate, combined with a self-assembled layer of ambient environmental dopants. We show that the substrate configuration controls the local doping region, and that the p-n junction behavior can be controlled with a single gate. Finally, we show that the ferroelectric substrate induces a hysteresis in the environmental doping which can be utilized to activate and deactivate the doping, yielding an “on-demand” p-n junction in graphene controlled by a single, universal backgate.
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Date Submitted: 7/27/16 12:00AM Date Published: 5/1/16 7:00AM
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Article Title: Strain-induced growth instability and nanoscale surface patterning in perovskite thin films
Authors: Shishir Pandya, Anoop R. Damodaran, Ruijuan Xu, Shang-Lin Hsu, Joshua C. Agar, Lane W. Martin
Keywords: surface patterning, surface, interfaces and thin films, synthesis and processing
Abstract: Despite extensive studies on the effects of epitaxial strain on the evolution of the lattice and properties of materials, considerably less work has explored the impact of strain on growth dynamics. In this work, we demonstrate a growth-mode transition from 2D-step flow to self-organized, nanoscale 3D-island formation in PbZr0.2Ti0.8O3/SrRuO3/SrTiO3 (001) heterostructures as the kinetics of the growth process respond to the evolution of strain. With increasing heterostructure thickness and misfit dislocation formation at the buried interface, a periodic, modulated strain field is generated that alters the adatom binding energy and, in turn, leads to a kinetic instability that drives a transition from 2D growth to ordered, 3D-island formation. The results suggest that the periodically varying binding energy can lead to inhomogeneous adsorption kinetics causing preferential growth at certain sites. This, in conjunction with the presence of an Ehrlich-Schwoebel barrier, gives rise to...
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Publication Location:
Article Title: Nonstoichiometry, Structure, and Properties of BiFeO
Authors: Liv R. Dedon, Sahar Saremi, Zuhuang Chen, Anoop R. Damodaran, Brent A. Apgar, Ran Gao, Lane W.
Keywords: BiFeO3, ferroelectric, devices
Abstract: We explore the effect of growth conditions on the cation and anion chemistry, electrical leakage, conduction mechanisms, and ferroelectric and dielectric behavior of BiFeO3. Although it is possible to produce single-phase, coherently strained films in all cases, small variations in the pulsed-laser deposition growth process, specifically the laser repetition rate and target composition, result in films with chemistries ranging from 10% Bi-deficiency to 4% Bi-excess and films possessing Bi gradients as large a 6% across the film thickness. Corresponding variations and gradients in the O chemistry are also observed. As a result of the varying film chemistry, marked differences in surface and domain morphology are observed wherein Bi-deficiency stabilizes atomically smooth surfaces and ordered stripe domains. Subsequent investigation of the current–voltage response reveals large differences in leakage current density arising from changes in both the overall stoichiometry and gradients. In

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Article Title: Frontiers in strain-engineered multifunctional ferroic materials
Authors: Joshua C. Agar, Shishir Pandya, Ruijuan Xu, Ajay K. Yadav, Zhiqi Liu, Thomas Angsten, Sahar Saremi,
Keywords: ferroic, multiferroic, strain engineering, functional
Abstract: Multifunctional, complex oxides capable of exhibiting highly-coupled electrical, mechanical, thermal, and magnetic susceptibilities have been pursued to address a range of salient technological challenges. Today, efforts are focused on addressing the pressing needs of a range of applications and identifying, understanding, and controlling materials with the potential for enhanced or novel responses. In this prospective, we highlight important developments in theoretical and computational techniques, materials synthesis, and characterization techniques. We explore how these new approaches could revolutionize our ability to discover, probe, and engineer these materials and provide a context for new arenas where these materials might make an impact.

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Article Title: Thin-film ferroelectric materials and their applications
Authors: Lane W. Martin, Andrew M. Rappe
Keywords: Electrical and electronic engineering; Electronic devices; Ferroelectrics and multiferroics; Materials for energy and catalysis; Surfaces, interfaces and thin films
Abstract: Ferroelectric materials, because of their robust spontaneous electrical polarization, are widely used in various applications. Recent advances in modelling, synthesis and characterization techniques are spurring unprecedented advances in the study of these materials. In this Review, we focus on thin-film ferroelectric materials and, in particular, on the possibility of controlling their properties through the application of strain engineering in conventional and unconventional ways. We explore how the study of ferroelectric materials has expanded our understanding of fundamental effects, enabled the discovery of novel phases and physics, and allowed unprecedented control of materials properties. We discuss several exciting possibilities for the development of new devices, including those in electronic, thermal and photovoltaic applications, and transduction sensors and actuators. We conclude with a brief survey of the different directions that the field may expand to over the coming ye
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Article Title: Ultrafast terahertz-field-driven ionic response in ferroelectric
Authors: F. Chen, Y. Zhu, S. Liu, Y. Qi, H. Y. Hwang, N. C. Brandt, J. Lu, F. Quirin, H. Enquist, P. Zalden, T. Hu,
Keywords: ultrafast, ferroelectric, BaTiO3, dynamics
Abstract: The dynamical processes associated with electric field manipulation of the polarization in a ferroelectric remain largely unknown but fundamentally determine the speed and functionality of ferroelectric materials and devices. Here we apply subpicosecond duration, single-cycle terahertz pulses as an ultrafast electric field bias to prototypical BaTiO3 ferroelectric thin films with the atomic-scale response probed by femtosecond x-ray-scattering techniques. We show that electric fields applied perpendicular to the ferroelectric polarization drive large-amplitude displacements of the titanium atoms along the ferroelectric polarization axis, comparable to that of the built-in displacements associated with the intrinsic polarization and incoherent across unit cells. This effect is associated with a dynamic rotation of the ferroelectric polarization switching on and then off on picosecond time scales. These transient polarization modulations are followed by long-lived vibrational heating...
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Article Title: Enhanced Electrical Resistivity and Properties via Ion Bombardment of Ferroelectric Thin Films
Authors: Sahar Saremi, Ruijuan Xu, Liv R. Dedon, Julia A. Mundy, Shang-Lin Hsu, Zuhuang Chen, Anoop R. Dar
Keywords: ferroelectric, PbTiO3, thin films, ion bombardment
Abstract: A novel approach to on-demand improvement of electronic properties in complex-oxide ferroelectrics is demonstrated whereby ion bombardment – commonly used in classic semiconductor materials – is applied to the PbTiO3 system. The result is deterministic reduction in leakage currents by 5 orders of magnitude, improved ferroelectric switching, and unprecedented insights into the nature of defects and intergap state evolution in these materials.
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Article Title: Pressurizing Field-Effect Transistors of Few-Layer MoS
Authors: Yabin Chen, Feng Ke, Penghong Ci, Changhyun Ko, Taegyun Park, Sahar Saremi, Huili Liu, Yeonbae L
Keywords: diamond anvil cell; field-effect transistor; h-BN dielectric; Hydrostatic pressure; MoS2
Abstract: Hydrostatic pressure applied using diamond anvil cells (DAC) has been widely explored to modulate physical properties of materials by tuning their lattice degree of freedom. Independently, electrical field is able to tune the electronic degree of freedom of functional materials via, for example, the field-effect transistor (FET) configuration. Combining these two orthogonal approaches would allow discovery of new physical properties and phases going beyond the known phase space. Such experiments are, however, technically challenging and have not been demonstrated. Herein, we report a feasible strategy to prepare and measure FETs in a DAC by lithographically patterning the nanodevices onto the diamond culet. Multiple-terminal FETs were fabricated in the DAC using few-layer MoS2 and BN as the channel semiconductor and dielectric layer, respectively. It is found that the mobility, conductance, carrier concentration, and contact conductance of MoS2 can all be significantly enhanced with pr
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Article Title: Direct Measurement of Pyroelectric and Electrocaloric Effects in Thin Films
Authors: Shishir Pandya, Joshua D. Wilbur, Bikram Bhatia, Anoop R. Damodaran, Christian Monachon, Arvind D
Keywords: pyroelectric, electrocaloric, thin films, measurement
Abstract: An understanding of polarization-heat interactions in pyroelectric and electrocaloric thin-film materials requires that the electrothermal response is reliably characterized. While most work, particularly in electrocalorics, has relied on indirect measurement protocols, here we report a direct technique for measuring both pyroelectric and electrocaloric effects in epitaxial ferroelectric thin films. We demonstrate an electrothermal test platform where localized high-frequency (approximately 1 kHz) periodic heating and highly sensitive thin-film resistance thermometry allow the direct measurement of pyrocurrents (<10?pA) and electrocaloric temperature changes (<2 mK) using the “2-omega” and an adapted “3-omega” technique, respectively. Frequency-domain, phase-sensitive detection permits the extraction of the pyrocurrent from the total current, which is often convoluted by thermally-stimulated currents. The wide-frequency-range measurements employed in this study further show the effect
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Article Title: Stability of Polar Vortex Lattice in Ferroelectric Superlattices
Authors: Zijian Hong, Anoop R. Damodaran, Fei Xue, Shang-Lin Hsu, Jason Britson, Ajay K. Yadav, Christopher
Keywords: Ferroelectric superlattices; geometric length scale; phase-field simulations; topological structures by design; ultrafine polar vortex
Abstract: A novel mesoscale state comprising of an ordered polar vortex lattice has been demonstrated in ferroelectric superlattices of PbTiO3/SrTiO3. Here, we employ phase-field simulations, analytical theory, and experimental observations to evaluate thermodynamic conditions and geometric length scales that are critical for the formation of such exotic vortex states. We show that the stability of these vortex lattices involves an intimate competition between long-range electrostatic, long-range elastic, and short-range polarization gradient-related interactions leading to both an upper and a lower bound to the length scale at which these states can be observed. We found that the critical length is related to the intrinsic domain wall width, which could serve as a simple intuitive design rule for the discovery of novel ultrafine topological structures in ferroic systems.
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Date Submitted: 8/10/17 12:00AM Date Published: 5/1/17 7:00AM
Publication Location:
Article Title: Large polarization gradients and temperature-stable responses in compositionally-graded ferroelectrics
Authors: Anoop R. Damodaran, Shishir Pandya, Yubo Qi, Shang-Lin Hsu, Shi Liu, Christopher Nelson, Arvind Da
Keywords: Ferroelectrics and multiferroics; Phase transitions and critical phenomena
Abstract: A range of modern applications require large and tunable dielectric, piezoelectric or pyroelectric response of ferroelectrics. Such effects are intimately connected to the nature of polarization and how it responds to externally applied stimuli. Ferroelectric susceptibilities are, in general, strongly temperature dependent, diminishing rapidly as one transitions away from the ferroelectric phase transition (TC). In turn, researchers seek new routes to manipulate polarization to simultaneously enhance susceptibilities and broaden operational temperature ranges. Here, we demonstrate such a capability by creating composition and strain gradients in Ba1?xSrxTiO3 films which result in spatial polarization gradients as large as 35??C?cm?2 across a 150?nm thick film. These polarization gradients allow for large dielectric permittivity with low loss (?r?775, tan??<0.05), negligible temperature-dependence (13% deviation over 500?°C) and high-dielectric tunability (greater than 70% across a 300?
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Journal: Chemistry of Materials
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.chemmater.7b02506
Volume: 29 Issue: 15 First Page #: 6544
Date Submitted: 8/10/17 12:00AM Date Published: 7/1/17 7:00AM
Publication Location:
Article Title: Ferroelectricity in Pb1+xZrO3 Thin Films
Authors: Ran Gao, Sebastian E. Reyes-Lillo, Ruijuan Xu, Arvind Dasgupta, Yongqi Dong, Liv R. Dedon, Jieun Ki
Keywords: antiferroelectric, PbZrO3, thin films, chemistry
Abstract: Antiferroelectric PbZrO3 is being considered for a wide range of applications where the competition between centrosymmetric and noncentrosymmetric phases is important to the response. Here, we focus on the epitaxial growth of PbZrO3 thin films and understanding the chemistry–structure coupling in Pb1+?ZrO3 (? = 0, 0.1, 0.2). High-quality, single-phase Pb1+?ZrO3 films are synthesized via pulsed-laser deposition. Although no significant lattice parameter change is observed in X-ray studies, electrical characterization reveals that while the PbZrO3 and Pb1.1ZrO3 heterostructures remain intrinsically antiferroelectric, the Pb1.2ZrO3 heterostructures exhibit a hysteresis loop indicative of ferroelectric response. Further X-ray scattering studies reveal strong quarter-order diffraction peaks in PbZrO3 and Pb1.1ZrO3 heterostructures indicative of antiferroelectricity, while no such peaks are observed for Pb1.2ZrO3 heterostructures. Density functional theory calculations suggest the large cati
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Volume: Issue: First Page #: 1702069
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Publication Location:
Article Title: Three-State Ferroelastic Switching and Large Electromechanical Responses in PbTiO
Authors: Anoop R. Damodaran, Shishir Pandya, Josh C. Agar, Ye Cao, Rama K. Vasudevan, Ruijuan Xu, Sahar
Keywords: PbTiO3, strain, thin films, electromechanical, ferroelastic
Abstract: Leveraging competition between energetically degenerate states to achieve large field-driven responses is a hallmark of functional materials, but routes to such competition are limited. Here, a new route to such effects involving domain-structure competition is demonstrated, which arises from strain-induced spontaneous partitioning of PbTiO3 thin films into nearly energetically degenerate, hierarchical domain architectures of coexisting c/a and a1/a2 domain structures. Using band-excitation piezoresponse force microscopy, this study manipulates and acoustically detects a facile interconversion of different ferroelastic variants via a two-step, three-state ferroelastic switching process (out-of-plane polarized c+ ? in-plane polarized a ? out-of-plane polarized c? state), which is concomitant with large nonvolatile electromechanical strains (?1.25%) and tunability of the local piezoresponse and elastic modulus (>23%). It is further demonstrated that deterministic, nonvolatile writing/era

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Journal: Nature Materials
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Date Submitted: 8/10/17 12:00AM Date Published: 8/1/17 7:00AM
Publication Location:
Article Title: Phase coexistence and electric-field control of toroidal order in oxide superlattices
Authors: A. R. Damodaran, J. D. Clarkson, Z. Hong, H. Liu, A. K. Yadav, C. T. Nelson, S.-L. Hsu, M. R. McCarter
Keywords: Ferroelectrics and multiferroics; Phase transitions and critical phenomena; Surfaces, interfaces and thin films
Abstract: Systems that exhibit phase competition, order parameter coexistence, and emergent order parameter topologies constitute a major part of modern condensed-matter physics. Here, by applying a range of characterization techniques, and simulations, we observe that in PbTiO3/SrTiO3 superlattices all of these effects can be found. By exploring superlattice period-, temperature- and field-dependent evolution of these structures, we observe several new features. First, it is possible to engineer phase coexistence mediated by a first-order phase transition between an emergent, low-temperature vortex phase with electric toroidal order and a high-temperature ferroelectric a1/a2 phase. At room temperature, the coexisting vortex and ferroelectric phases form a mesoscale, fibre-textured hierarchical superstructure. The vortex phase possesses an axial polarization, set by the net polarization of the surrounding ferroelectric domains, such that it possesses a multi-order-parameter state and belongs to

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Volume: 8 Issue: 1 First Page #:
Date Submitted: 7/24/18 12:00AM Date Published: 11/1/17 7:00AM
Publication Location:
Article Title: Quantification of flexoelectricity in PbTiO3/SrTiO3 superlattice polar vortices using machine learning and phase-field modeling
Authors: Q. Li, C. T. Nelson, S.-L. Hsu, A. R. Damodaran, L.-L. Li, A. K. Yadav, M. McCarter, L. W. Martin, R. Ra
Keywords: flexoelectric, superlattices, ferroelectric
Abstract: Flexoelectricity refers to electric polarization generated by heterogeneous mechanical strains, namely strain gradients, in materials of arbitrary crystal symmetries. Despite more than 50 years of work on this effect, an accurate identification of its coupling strength remains an experimental challenge for most materials, which impedes its wide recognition. Here, we show the presence of flexoelectricity in the recently discovered polar vortices in PbTiO3/SrTiO3 superlattices based on a combination of machine-learning analysis of the atomic-scale electron microscopy imaging data and phenomenological phase-field modeling. By scrutinizing the influence of flexocoupling on the global vortex structure, we match theory and experiment using computer vision methodologies to determine the flexoelectric coefficients for PbTiO3 and SrTiO3. Our findings highlight the inherent, nontrivial role of flexoelectricity in the generation of emergent complex polarization morphologies and demonstrate a...
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Journal: Physical Review Materials
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Volume: 1 Issue: 6 First Page #:
Date Submitted: 7/24/18 12:00AM Date Published: 11/1/17 2:00PM
Publication Location:
Article Title: Structural imaging of nanoscale phonon transport in ferroelectrics excited by metamaterial-enhanced terahertz fields
Authors: Yi Zhu, Frank Chen, Joonkyu Park, Kiran Sasikumar, Bin Hu, Anoop R. Damodaran, Il Woong Jung, Ma
Keywords: ferroelectric, terahertz, ultrafast
Abstract: Nanoscale phonon transport is a key process that governs thermal conduction in a wide range of materials and devices. Creating controlled phonon populations by resonant excitation at terahertz (THz) frequencies can drastically change the characteristics of nanoscale thermal transport and allow a direct real-space characterization of phonon mean-free paths. Using metamaterial-enhanced terahertz excitation, we tailored a phononic excitation by selectively populating low-frequency phonons within a nanoscale volume in a ferroelectric BaTiO3 thin film. Real-space time-resolved x-ray diffraction microscopy following THz excitation reveals ballistic phonon transport over a distance of hundreds of nm, two orders of magnitude longer than the averaged phonon mean-free path in BaTiO3. On longer length scales, diffusive phonon transport dominates the recovery of the transient strain response, largely due to heat conduction into the substrate. The measured real-space phonon transport can be...
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Volume: 111 Issue: 25 First Page #: 253501
Date Submitted: 7/24/18 12:00AM Date Published: 12/1/17 8:00AM
Publication Location:
Article Title: Differential voltage amplification from ferroelectric negative capacitance
Authors: Asif I. Khan, Michael Hoffmann, Korok Chatterjee, Zhongyuan Lu, Ruijuan Xu, Claudy Serrao, Samuel S
Keywords: ferroelectric, negative capacitance, devices
Abstract: We demonstrate that a ferroelectric can cause a differential voltage amplification without needing an external energy source. As the ferroelectric switches from one polarization state to the other, a transfer of energy takes place from the ferroelectric to the dielectric, determined by the ratio of their capacitances, which, in turn, leads to the differential amplification. This amplification is very different in nature from conventional inductor-capacitor based circuits where an oscillatory amplification can be observed. The demonstration of differential voltage amplification from completely passive capacitor elements only has fundamental ramifications for next generation electronics.
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Volume: 5 Issue: 3 First Page #: 1700991
Date Submitted: 7/24/18 12:00AM Date Published: 2/1/18 12:00AM
Publication Location:
Article Title: Electronic Transport and Ferroelectric Switching in Ion-Bombarded, Defect-Engineered BiFeO
Authors: Sahar Saremi, Ruijuan Xu, Liv R. Dedon, Ran Gao, Anirban Ghosh, Arvind Dasgupta, Lane W. Martin
Keywords: ferroelectric, defects, BiFeO3
Abstract: Despite continued interest in the multiferroic BiFeO3 for a diverse range of applications, use of this material is limited by its poor electrical leakage. This work demonstrates some of the most resistive BiFeO3 thin films reported to date via defect engineering achieved via high?energy ion bombardment. High leakage in as?grown BiFeO3 thin films is shown to be due to the presence of moderately shallow isolated trap states, which form during growth. Ion bombardment is shown to be an effective way to reduce this free carrier transport (by up to ?4 orders of magnitude) by trapping the charge carriers in bombardment?induced, deep?lying defect complexes and clusters. The ion bombardment is also found to give rise to an increased resistance to switching as a result of an increase in defect concentration. This study demonstrates a systematic ion?dose?dependent increase in the coercivity, extension of the defect?related creep regime, increase in the pinning activation energy, decrease in the..
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Publication Identifier Type: ISSN Publication Identifier: 0002-7812
Volume: 97 Issue: 1 First Page #: 16
Date Submitted: 7/24/18 12:00AM Date Published: 1/24/17 6:20PM
Publication Location:
Article Title: New facets for the role of defects in ceramics
Authors: S. Saremi, R. Xu, L. R. Dedon, L. W. Martin
Keywords: ferroelectric, defects, properties
Abstract: Armed with advances in our ability to synthesize, characterize, and model materials, it may be time to redefine the negative connotation surrounding defects in ceramic materials. But can defects really shine as the “good guys” in materials science?
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Volume: 29 Issue: 15 First Page #: 155302
Date Submitted: 7/24/18 12:00AM Date Published: 4/1/18 7:00AM
Publication Location:
Article Title: Subtractive fabrication of ferroelectric thin films with precisely controlled thickness
Authors: Anton V Ievlev, Marius Chyasnavichyus, Donovan N Leonard, Joshua C Agar, Gabriel A Velarde, Lane
Keywords: ferroelectric, defects, properties
Abstract: The ability to control thin-film growth has led to advances in our understanding of fundamental physics as well as to the emergence of novel technologies. However, common thin-film growth techniques introduce a number of limitations related to the concentration of defects on film interfaces and surfaces that limit the scope of systems that can be produced and studied experimentally. Here, we developed an ion-beam based subtractive fabrication process that enables creation and modification of thin films with pre-defined thicknesses. To accomplish this we transformed a multimodal imaging platform that combines time-of-flight secondary ion mass spectrometry with atomic force microscopy to a unique fabrication tool that allows for precise sputtering of the nanometer-thin layers of material. To demonstrate fabrication of thin-films with in situ feedback and control on film thickness and functionality we systematically studied thickness dependence of ferroelectric switching of lead-zirconate
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Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.analchem.7b05225
Volume: 90 Issue: 5 First Page #: 3475
Date Submitted: 7/24/18 12:00AM Date Published: 1/1/18 8:00AM
Publication Location:
Article Title: Chemical Phenomena of Atomic Force Microscopy Scanning
Authors: Anton V. Ievlev, Chance Brown, Matthew J. Burch, Joshua C. Agar, Gabriel A. Velarde, Lane W. Martin,
Keywords: atomic force microscope, surfaces, chemistry
Abstract: Atomic force microscopy is widely used for nanoscale characterization of materials by scientists worldwide. The long-held belief of ambient AFM is that the tip is generally chemically inert but can be functionalized with respect to the studied sample. This implies that basic imaging and scanning procedures do not affect surface and bulk chemistry of the studied sample. However, an in-depth study of the confined chemical processes taking place at the tip–surface junction and the associated chemical changes to the material surface have been missing as of now. Here, we used a hybrid system that combines time-of-flight secondary ion mass spectrometry with an atomic force microscopy to investigate the chemical interactions that take place at the tip–surface junction. Investigations showed that even basic contact mode AFM scanning is able to modify the surface of the studied sample. In particular, we found that the silicone oils deposited from the AFM tip into the scanned regions and spread
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Date Submitted: 7/24/18 12:00AM Date Published: 4/1/18 7:00AM
Publication Location:
Article Title: Pyroelectric energy conversion with large energy and power density in relaxor ferroelectric thin films
Authors: Shishir Pandya, Joshua Wilbur, Jieun Kim, Ran Gao, Arvind Dasgupta, Chris Dames, Lane W. Martin
Keywords: ferroelectric, pyroelectric, energy conversion, waste heat
Abstract: The need for efficient energy utilization is driving research into ways to harvest ubiquitous waste heat. Here, we explore pyroelectric energy conversion from low-grade thermal sources that exploits strong field- and temperature-induced polarization susceptibilities in the relaxor ferroelectric 0.68Pb(Mg1/3Nb2/3)O3–0.32PbTiO3. Electric-field-driven enhancement of the pyroelectric response (as large as ?550??C?m?2?K?1) and suppression of the dielectric response (by 72%) yield substantial figures of merit for pyroelectric energy conversion. Field- and temperature-dependent pyroelectric measurements highlight the role of polarization rotation and field-induced polarization in mediating these effects. Solid-state, thin-film devices that convert low-grade heat into electrical energy are demonstrated using pyroelectric Ericsson cycles, and optimized to yield maximum energy density, power density and efficiency of 1.06?J?cm?3, 526?W?cm?3 and 19% of Carnot, respectively; the highest values...
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Journal: ACS Nano
Publication Identifier Type: DOI Publication Identifier: 10.1021/acsnano.8b01399
Volume: 12 Issue: 5 First Page #: 4736
Date Submitted: 7/24/18 12:00AM Date Published: 4/1/18 7:00AM
Publication Location:
Article Title: Reducing Coercive-Field Scaling in Ferroelectric Thin Films
Authors: Ruijuan Xu, Ran Gao, Sebastian E. Reyes-Lillo, Sahar Saremi, Yongqi Dong, Hongling Lu, Zuhuang Ch
Keywords: ferroelectric, low voltage, scaling law
Abstract: The desire for low-power/voltage operation of devices is driving renewed interest in understanding scaling effects in ferroelectric thin films. As the dimensions of ferroelectrics are reduced, the properties can vary dramatically, including the robust scaling relationship between coercive field (Ec) and thickness (d), also referred to as the Janovec–Kay–Dunn (JKD) law, wherein Ec ? d–2/3. Here, we report that whereas (001)-oriented heterostructures follow JKD scaling across the thicknesses range of 20–330 nm, (111)-oriented heterostructures of the canonical tetragonal ferroelectric PbZr0.2Ti0.8O3 exhibit a deviation from JKD scaling wherein a smaller scaling exponent for the evolution of Ec is observed in films of thickness ? 165 nm. X-ray diffraction reveals that whereas (001)-oriented heterostructures remain tetragonal for all thicknesses, (111)-oriented heterostructures exhibit a transition from tetragonal-to-monoclinic symmetry in films of thickness ? 165 nm as a result of the...
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Volume: 120 Issue: 22 First Page #:
Date Submitted: 7/24/18 12:00AM Date Published: 5/1/18 7:00AM
Publication Location:
Article Title: Intrinsic Two-Dimensional Ferroelectricity with Dipole Locking
Authors: Jun Xiao, Hanyu Zhu, Ying Wang, Wei Feng, Yunxia Hu, Arvind Dasgupta, Yimo Han, Yuan Wang, Dav
Keywords: ferroelectric, In2Se2, 2D materials
Abstract: Out-of-plane ferroelectricity with a high transition temperature in ultrathin films is important for the exploration of new domain physics and scaling down of memory devices. However, depolarizing electrostatic fields and interfacial chemical bonds can destroy this long-range polar order at two-dimensional (2D) limit. Here we report the experimental discovery of the locking between out-of-plane dipoles and in-plane lattice asymmetry in atomically thin In2Se3 crystals, a new stabilization mechanism leading to our observation of intrinsic 2D out-of-plane ferroelectricity. Through second harmonic generation spectroscopy and piezoresponse force microscopy, we found switching of out-of-plane electric polarization requires a flip of nonlinear optical polarization that corresponds to the inversion of in-plane lattice orientation. The polar order shows a very high transition temperature (?700K) without the assistance of extrinsic screening. This finding of intrinsic 2D ferroelectricity...
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Date Submitted: 7/24/18 12:00AM Date Published: 5/1/18 7:00AM
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Article Title: Machine Detection of Enhanced Electromechanical Energy Conversion in PbZr
Authors: Joshua C. Agar, Ye Cao, Brett Naul, Shishir Pandya, Stéfan van der Walt, Aileen I. Luo, Joshua T. Mah
Keywords: ferroelectric, domain structure, machine learning
Abstract: Many energy conversion, sensing, and microelectronic applications based on ferroic materials are determined by the domain structure evolution under applied stimuli. New hyperspectral, multidimensional spectroscopic techniques now probe dynamic responses at relevant length and time scales to provide an understanding of how these nanoscale domain structures impact macroscopic properties. Such approaches, however, remain limited in use because of the difficulties that exist in extracting and visualizing scientific insights from these complex datasets. Using multidimensional band?excitation scanning probe spectroscopy and adapting tools from both computer vision and machine learning, an automated workflow is developed to featurize, detect, and classify signatures of ferroelectric/ferroelastic switching processes in complex ferroelectric domain structures. This approach enables the identification and nanoscale visualization of varied modes of response and a pathway to statistically...
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Volume: 2 Issue: 8 First Page #:
Date Submitted: 8/15/19 12:00AM Date Published: 8/1/18 7:00AM
Publication Location:
Article Title: Local control of defects and switching properties in ferroelectric thin films
Authors: Sahar Saremi, Ruijuan Xu, Frances I. Allen, Joshua Maher, Joshua C. Agar, Ran Gao, Peter Hosemanr
Keywords: defects, ferroelectrics, thin films
Abstract: Electric-field switching of polarization is the building block of a wide variety of ferroelectric devices. In turn, understanding the factors affecting ferroelectric switching and developing routes to control it are of greattechnological significance. Thiswork provides systematic experimental evidence of the role of defects in affecting ferroelectric-polarization switching and utilizes the ability to deterministically create and spatially locate point defects in PbZr0.2Ti0.8O3 thin films via focused-helium-ion bombardment and the subsequent defect-polarization coupling as a knob for on-demand control of ferroelectric switching (e.g., coercivity and imprint). At intermediate ion doses (0.22–2.2 × 1014 ions cm?2), the dominant defects (isolated point defects and small clusters) show a weak interaction with domain walls (pinning potentials from 200–500KMVcm?1), resulting in small and symmetric changes in the coercive field.At high doses (0.22–1 × 1015 ions cm?2), on the other hand, the...
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Date Submitted: 8/15/19 12:00AM Date Published: 8/1/18 7:00AM
Publication Location:
Article Title: Resonant domain-wall-enhanced tunable microwave ferroelectrics
Authors: Zongquan Gu, Shishir Pandya, Atanu Samanta, Shi Liu, Geoffrey Xiao, Cedric J. G. Meyers, Anoop R. D
Keywords: ferroelectrics, domain walls, microwave resonance
Abstract: Ordering of ferroelectric polarization1 and its trajectory in response to an electric field2 are essential for the operation of non-volatile memories3, transducers4 and electro-optic devices5. However, for voltage control of capacitance and frequency agility in telecommunication devices, domain walls have long been thought to be a hindrance because they lead to high dielectric loss and hysteresis in the device response to an applied electric field6. To avoid these effects, tunable dielectrics are often operated under piezoelectric resonance conditions, relying on operation well above the ferroelectric Curie temperature7, where tunability is compromised. Therefore, there is an unavoidable trade-off between the requirements of high tunability and low loss in tunable dielectric devices, which leads to severe limitations on their figure of merit. Here we show that domain structure can in fact be exploited to obtain ultralow loss and exceptional frequency selectivity without piezoelectric..
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Publication Identifier Type: DOI Publication Identifier: 10.1039/C8TC02725K
Volume: 6 Issue: 40 First Page #: 10751
Date Submitted: 8/15/19 12:00AM Date Published:
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Article Title: Nonstoichiometry, structure, and properties of Ba
Authors: Arvind Dasgupta, Sahar Saremi, Xu Ruijuan, Liv R. Dedon, Shishir Pandya, Anoop R. Damodaran, Lane
Keywords: ferroelectric, BaTiO3, thin films, defects
Abstract: The effects of growth conditions on the chemistry, structure, electrical leakage, dielectric response, and ferroelectric behavior of Ba1-xTiOy thin films are explored. Although single-phase, coherently-strained films are produced in all cases, small variations in the laser fluence during pulsed-laser deposition growth result in films with chemistries ranging from BaTiO3 to Ba0.93TiO2.87. As the laser fluence increases, the films become more barium deficient and the out-of-plane lattice parameter expands (as much as 5.4% beyond the expected value for Ba0.93TiO2.87 films). Stoichiometric BaTiO3 films are found to be three orders of magnitude more conducting than Ba0.93TiO2.87 films and the barium-deficient films exhibit smaller low-field permittivity, lower loss tangents, and higher dielectric maximum temperatures. Although large polarization is observed in all cases, large built-in potentials (shifted loops) and hysteresis-loop pinching are present in barium-deficient films – suggesting
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Volume: 52 Issue: 1 First Page #: 013001
Date Submitted: 8/15/19 12:00AM Date Published: 1/1/19 8:00AM
Publication Location:
Article Title: The 2019 materials by design roadmap
Authors: Kirstin Alberi, Marco Buongiorno Nardelli, Andriy Zakutayev, Lubos Mitas, Stefano Curtarolo, Anubhav J
Keywords: density functional theory, materials genome initative, materials design, high-throughput methods, energy applications
Abstract: Advances in renewable and sustainable energy technologies critically depend on our ability to design and realize materials with optimal properties. Materials discovery and design efforts ideally involve close coupling between materials prediction, synthesis and characterization. The increased use of computational tools, the generation of materials databases, and advances in experimental methods have substantially accelerated these activities. It is therefore an opportune time to consider future prospects for materials by design approaches. The purpose of this Roadmap is to present an overview of the current state of computational materials prediction, synthesis and characterization approaches, materials design needs for various technologies, and future challenges and opportunities that must be addressed. The various perspectives cover topics on computational techniques, validation, materials databases, materials informatics, high-throughput combinatorial methods, advanced characterizat
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Date Submitted: 8/15/19 12:00AM Date Published: 10/1/18 7:00AM
Publication Location:
Article Title: Perspective: Emergent topologies in oxide superlattices
Authors: Sujit Das, Anirban Ghosh, Margaret R. McCarter, Shang-Lin Hsu, Yun-Long Tang, Anoop R. Damodara
Keywords: ferroelectrics, superlattices, emergent
Abstract: The ability to synthesize high-quality, complex-oxide heterostructures has created a veritable playground in which to explore emergent phenomena and exotic phases which arise from the interplay of spin, charge, orbital, and lattice degrees of freedom. Of particular interest is the creation of artificial heterostructures and superlattices built from two or more materials. Through such approaches, it is possible to observe new phases and phenomena that are not present in the parent materials alone. This is especially true in ferroelectric materials where the appropriate choice of superlattice constituents can lead to structures with complex phase diagrams and rich physics. In this article, we review and explore future directions in such ferroic superlattices wherein recent studies have revealed complex emergent polarization topologies, novel states of matter, and intriguing properties that arise from our ability to manipulate materials with epitaxial strain, interfacial coupling and inte
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Article Title: Pyroelectric and electrocaloric effects in ferroelectric silicon-doped hafnium oxide thin films
Authors: Shishir Pandya, Gabriel Velarde, Lei Zhang, Lane W. Martin
Keywords: HfO2, ferroelectric, pyroelectric, electrocaloric, thin film
Abstract: The emergent ferroelectricity in HfO2-based systems has attracted significant attention as this simple binary high-k dielectric now offers the possibility of nonvolatile function. In this work we employ zero-field and field-dependent pyroelectricity to show that thin films of silicon-doped HfO2 do exhibit a broken-inversion symmetry and are indeed ferroelectric. In addition, the pyroelectric response is found to exhibit a wake-up behavior akin to the wake-up phenomenon observed in the ferroelectric polarization with electric-field cycling. Using polarization-electric field hysteresis measurements, this wake-up phenomenon is attributed to the presence of defect dipoles which explains the measured pyroelectric response. Finally, direct electrocaloric measurements are performed on these silicon-doped HfO2 thin films, revealing an electrocaloric coefficient ?4 times larger in magnitude than that expected for the measured pyroelectric coefficient. This enhancement is explained using the pla
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Journal: Advanced Functional Materials
Publication Identifier Type: DOI Publication Identifier: 10.1002/adfm.201804258
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Date Submitted: 8/15/19 12:00AM Date Published: 2/1/19 8:00AM
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Article Title: Relaxor Behavior in Ordered Lead Magnesium Niobate (PbMg
Authors: Smitha Shetty, Anoop Damodaran, Ke Wang, Yakun Yuan, Venkat Gopalan, Lane Martin, Susan Trolier
Keywords: relaxor, thin films, ferroelectric
Abstract: The local compositional heterogeneity associated with the short-range ordering of Mg and Nb in PbMg1/3Nb2/3O3 (PMN) is correlated with its characteristic relaxor ferroelectric behavior. Fully ordered PMN is not prepared as a bulk material. This work examines the relaxor behavior in PMN thin films grown at temperatures below 1073 K by artificially reducing the degree of disorder via synthesis of heterostructures with alternate layers of Pb(Mg2/3Nb1/3)O3 and PbNbO3, as suggested by the random-site model. 100 nm thick, phase-pure films are grown epitaxially on (111) SrTiO3 substrates using alternate target timed pulsed-laser deposition of Pb (Mg2/3Nb1/3)O3 and PbNbO3 targets with 20% excess Pb. Selected area electron diffraction confirms the emergence of (1/2, 1/2, 1/2) superlattice spots with randomly distributed ordered domains as large as ?150 nm. These heterostructures exhibit a dielectric constant of 800, loss tangents of ?0.03 and 2× remanent polarization of ?11 ?C cm?2 at room tempe
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Journal: Advanced Materials
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Date Submitted: 8/15/19 12:00AM Date Published: 2/1/19 8:00AM
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Article Title: Understanding the Role of Ferroelastic Domains on the Pyroelectric and Electrocaloric Effects in Ferroelectric Thin Films
Authors: Shishir Pandya, Gabriel A. Velarde, Ran Gao, Arnoud S. Everhardt, Joshua D. Wilbur, Ruijuan Xu, Josh
Keywords: domain walls, ferroelectric, pyroelectric, electrocaloric
Abstract: Temperature- and electric-field-induced structural transitions in a polydomain ferroelectric can have profound effects on its electrothermal susceptibilities. Here, the role of such ferroelastic domains on the pyroelectric and electrocaloric response is experimentally investigated in thin films of the tetragonal ferroelectric PbZr0.2Ti0.8O3. By utilizing epitaxial strain, a rich set of ferroelastic polydomain states spanning a broad thermodynamic phase space are stabilized. Using temperature-dependent scanningprobe microscopy, X-ray diffraction, and high-frequency phase-sensitive pyroelectric measurements, the propensity of domains to reconfigure under a temperature perturbation is quantitatively studied. In turn, the “extrinsic” contributions to pyroelectricity exclusively due to changes between the ferroelastic domain population is elucidated as a function of epitaxial strain. Further, using highly sensitive thin-film resistive thermometry, direct electrocaloric temperature changes a
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Date Submitted: 8/15/19 12:00AM Date Published: 3/1/19 8:00AM
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Article Title: Kinetic control of tunable multi-state switching in ferroelectric thin films
Authors: R. Xu, S. Liu, S. Saremi, R. Gao, J. J. Wang, Z. Hong, H. Lu, A. Ghosh, S. Pandya, E. Bonturim, Z. H. C
Keywords: ferroelectric, thin films, multi-state, switching
Abstract: Deterministic creation of multiple ferroelectric states with intermediate values of polarization remains challenging due to the inherent bi-stability of ferroelectric switching. Here we show the ability to select any desired intermediate polarization value via control of the switching pathway in (111)-oriented PbZr0.2Ti0.8O3 films. Such switching phenomena are driven by kinetic control of the volume fraction of two geometrically different domain structures which are generated by two distinct switching pathways: one direct, bipolar-like switching and another multi-step switching process with the formation of a thermodynamically-stable intermediate twinning structure. Such control of switching pathways is enabled by the competition between elastic and electrostatic energies which favors different types of ferroelastic switching that can occur. Overall, our work demonstrates an alternative approach that transcends the inherent bi-stability of ferroelectrics to create non-volatile, determi
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Date Submitted: 8/15/19 12:00AM Date Published: 4/1/19 7:00AM
Publication Location:
Article Title: Epitaxial Strain Control of Relaxor Ferroelectric Phase Evolution
Authors: Jieun Kim, Hiroyuki Takenaka, Yubo Qi, Anoop R. Damodaran, Abel Fernandez, Ran Gao, Margaret R.
Keywords: relaxor, epitaxial strain, ferroelectric, thin film
Abstract: Understanding and ultimately controlling the large electromechanical effects in relaxor ferroelectrics requires intimate knowledge of how the local-polar order evolves under applied stimuli. Here, the biaxial-strain-induced evolution of and correlations between polar structures and properties in epitaxial films of the prototypical relaxor ferroelectric 0.68PbMg1/3Nb2/3O3–0.32PbTiO3 are investigated. X-ray diffuse-scattering studies reveal an evolution from a butterfly- to disc-shaped pattern and an increase in the correlation-length from ?8 to ?25 nm with increasing compressive strain. Molecular-dynamics simulations reveal the origin of the changes in the diffuse-scattering patterns and that strain induces polarization rotation and the merging of the polar order. As the magnitude of the strain is increased, relaxor behavior is gradually suppressed but is not fully quenched. Analysis of the dynamic evolution of dipole alignment in the simulations reveals that, while, for most unit-cell
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Publication Location:
Article Title: New approach to waste-heat energy harvesting: pyroelectric energy conversion
Authors: Shishir Pandya, Gabriel Velarde, Lei Zhang, Joshua D. Wilbur, Andrew Smith, Brendan Hanrahan, Chris
Keywords: pyroelectric, energy conversion, waste-heat
Abstract: Harvesting waste heat for useful purposes is an essential component of improving the efficiency of primary energy utilization. Today, approaches such as pyroelectric energy conversion are receiving renewed interest for their ability to turn wasted energy back into useful energy. From this perspective, the need for these approaches, the basic mechanisms and processes underlying their operation, and the material and device requirements behind pyroelectric energy conversion are reviewed, and the potential for advances in this area is also discussed.
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CONFERENCE PAPERS:

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Conference Name: 2018 IEEE International Electron Devices Meeting (IEDM)
Date Received: 15-Aug-2019 Conference Date: 01-Dec-2018 Date Published:
Conference Location: San Francisco, CA
Paper Title: Experimental Demonstration of Ferroelectric Spiking Neurons for Unsupervised Clustering
Authors: Zheng Wang, Brian Crafton, Jorge Gomez, Ruijuan Xu, Aileen Luo, Zoran Krivokapic, Lane Martin, Sum
Acknowledged Federal Support: **Y**

DISSERTATIONS:

Publication Type: Thesis or Dissertation
Institution:
Date Received: 10-Aug-2015 Completion Date:
Title: Epitaxial Strain Induced Phase Competition in Perovskite Ferroelectrics
Authors:
Acknowledged Federal Support:

***Major Goals** – A description of major goals of the project; are determined by the agreement between the researcher and the sponsor (8000 characters)

The objectives of this research program are to develop a deeper understanding of the physics and thermodynamics of thermo-electrical responses in complex oxide materials with special attention to producing enhanced pyroelectric and electrocaloric effects. In particular, the program will focus on the application of such effects for advanced solid-state cooling devices. This will be achieved by implementation of a *combined modeling, synthesis, characterization,* and *device fabrication* approach and the development of a unique materials design protocol. In particular the program will work to answer the central question: **what are the key materials properties that provide us with the ability to manipulate and control the temperature- and field-dependence of entropic changes required for thermo-electrical response in ferroic oxides?** This will include a unique study of multiferroic materials and the development of new routes to maximize entropic changes in materials. This will enable large pyroelectric and electrocaloric responses and, in turn, enhanced cooling capacity in devices. The program will address such challenges by incorporating the PI's expertise in creating and characterizing epitaxial oxide thin-film heterostructures into a multi-faceted study of thermo-electrical properties and physics. The objectives are to expand the understanding of the fundamental mechanisms of these effects, to develop predictive capabilities for responses in real thin films, to probe the properties and ultimate performance of these materials, and to demonstrate first generation devices.

Specific Objectives and Aims

- Investigate, for the first time, the potential of coupled order parameters in multiferroics/ magnetoelectrics to enhance thermo-electrical responses via so-called *magneto-electro-caloric* and *pyro-electric-magnetic* effects.
- Utilize epitaxial thin-film synthesis techniques to exerting control over phase transformations, ferroic domain structures, and interfaces in multiferroic and novel frustrated ferroelectric heterostructures that will enable enhanced thermo-electrical responses.
- Expand phenomenological models of these thermodynamic properties beyond 1D approaches to include polydomain structures, multi-layered heterostructures, compositional and strain gradients, and other features common in real films.
- Overcome inadequacies in characterization of such properties through the development of new techniques to provide direct measurement of temperature changes.
- Demonstrate rudimentary solid-state refrigeration devices based on ferroic and multiferroic materials – including work towards cooling to 70K and below.

***Accomplished under Goals** – A description of what was accomplished under the goals during the reporting period; text only (8000 characters). Specifically cover: 1) Major activities, 2) Specific objectives, 3) significant results including major findings, developments, or conclusions (both positive and negative), and 4) key outcomes or other achievements. Include discussion of stated goals not met.

During the 6 month no-cost extension (NCE), a number of important accomplishments were completed including publication of 11 peer-review papers including papers in *Advanced Materials* (1), *Nano Letters* (1), *Nature Communications* (2), *Advanced Functional Materials* (1), and others. The major accomplishments can be summarized as follows

1) **Advances in the study of electro-thermal effects in ferroic thin films** – We continued our contributions in this space, including we directly measuring the magnitude and sign of the intrinsic, extrinsic, dielectric, and secondary pyroelectric contributions to the total pyroelectric response as a function of chemistry in thin films of $PbZr_{1-x}Ti_xO_3$ (x = 0.40, 0.48, 0.60, and 0.80) using phase-sensitive frequency and applied dc-bias methods [*ACS Appl. Mater. Inter.* **11**, 35146 (2019)]. Additionally, we measured the nature of pyroelectric response in thin films of the multiferroic $Bi_{1-x}La_xFeO_3$ (x = 0–0.45) wherein lanthanum substitution results in a chemically induced lowering of the ferroelectric-to-paraelectric and structural-phase transition and a 100% increase in the room temperature pyroelectric response [*APL Mater.* **7**, 111111 (2019)].

2) **High-performance materials: Relaxor ferroelectrics** – We also developed novel understanding in complex relaxor materials including probing the effect of intrinsic point defects on relaxor properties of $0.68PbMg_{1/3}Nb_{2/3}O_3$-$0.32PbTiO_3$ thin films via ex post facto ion bombardment. Increasing defect concentration was found to weaken relaxor character because of the strong interactions between defect dipoles and the polarization [*Phys. Rev. Lett.* **123**, 207602 (2019)]. Also, we studied finite-size effects on relaxor order in 7-70-nm-thick films of $PbSc_{0.5}Ta_{0.5}O_3$ wherein below ~ 30 nm, suppression of relaxor order rapidly accelerates corresponding to the polarization correlations lengths being approximately the same as the film thickness [*Phys. Rev. B* **101**, 094102 (2020), Editor's Suggestion].
3) **Emergent function from novel approaches** – We showed the ability to produce large ferroelectric polarization and dielectric permittivity $(PbZr_{0.8}Ti_{0.2}O_3)_n/(PbZr_{0.4}Ti_{0.6}O_3)_{2n}$ superlattices. In intermediate-period (n = 4) superlattices we found evidence of layers acting like both the parents and the MPB composition – giving rise to the novel properties [*Adv. Electron. Mater.* 1901395 (2020)]. We also leveraged machine-learning approaches like deep sequence-to-sequence autoencoders to automate the extraction of latent features of nanoscale ferroelectric switching from piezoresponse force spectroscopy. We classified and quantified nanoscale-switching mechanisms and identified elastic hardening events which are associated with the nucleation and growth of charged domain walls [*Nature Commun.* **10**, 4809 (2019)].

Over the duration of the full program, we produced 70 publications (13, 10, 12, 12, 12, and 11 in Years 1, 2, 3, 4, 5, and the NCE, respectively) as of the writing of this report. This includes articles in *Nature* (1), *Nature Materials* (4), *Advanced Materials* (10), *Nature Communications* (7), ACS Nano (3), Nano Letters (3), Physical Review Letters (1), *Advanced Functional Materials* (2), and many others. The major contributions of this work over the years include, but are not limited to, impacts in:

1) ***Advances in the study of electro-thermal effects in ferroic thin films*** – From the development of novel ways to measure both pyroelectric and electrocaloric responses in thin-film materials with higher precision than ever done before to demonstrating record-breaking pyroelectric energy conversion from low-grade thermal sources we have leveraged our fundamental contributions in measurement science to make impact in our ability to produce and control materials in thoughtful ways. In turn, we have provided the most indepth studies of such properties in a range of materials. These included classical ferroelectrics, like $PbZr_{0.2}Ti_{0.8}O_3$ where we have quantified the "extrinsic" contributions to pyroelectricity due to changes between the ferroelastic domain population among other effects. We have also completed direct electrocaloric measurements for the first time and highlighted that pyroelectric and electrocaloric effects are enhanced due to the exact-opposite effects from the extrinsic contributions under tensile strain. We have also probed non-classical materials like silicon-doped HfO_2 and proven that it is indeed polar and ferroelectric, has pyroelectric response, and that the electrocaloric response is larger than expected due to defects which can contribute to configurational or dipolar entropy. This program enable the PI to be a world leader in this space.
2) ***Rewriting the role of domains/domain walls in material function*** – From day one, we have provided fundamental know-how as to the role of domain walls in the response of ferroelectric materials. This includes demonstrating novel domain-wall-based effects that can contribute to large dielectric response, developing new orientation-dependent phenomenological models to probe domain structures and properties in ferroelectrics, identifying new pathways to ferroelectric switching in (111)-oriented ferroelectrics, used compositional gradients in films to tune the energy landscape for ferroelectric domains such that novel function – including spring-like responses and large electromechanical effects, and even shown that domain walls, which have long been thought to be a hindrance because they lead to high dielectric loss and hysteresis in the device response to an applied electric field, can be used for good in creating high-performance and tunable microwave dielectrics.
3) ***Design and understanding of emergent polarization physics*** – A theme of our work has been the identification of routes to produce exotic, unexpected, and greatly enhanced stimuli-induced effects in ferroic materials. We have produced complex topologies of electrical polarization - namely, nanometer-scale vortex arrays that are reminiscent of rotational spin topologies - by making use of the competition between charge, orbital, and lattice degrees of freedom in superlattices of alternating $PbTiO_3$ and $SrTiO_3$. In turn, we showed that these vortices can coexist

with classical ferroelectric domain structures and that they interconversion is mediated by a first-order phase transition. At room temperature, the coexisting vortex and ferroelectric phases form a mesoscale, fiber-textured hierarchical superstructure and the vortex phase possesses an axial polarization, set by the net polarization of the surrounding ferroelectric domains, such that it possesses a multi-order-parameter state and belongs to a class of gyrotropic electrotoroidal compounds. Application of electric fields permits interconversion between the vortex and the ferroelectric phases concomitant with order-of-magnitude changes in piezoelectric and nonlinear optical responses. Finally, using novel growth approaches, such as compositional gradients, we produced large spatial gradients in ferroelectric polarization (changes of 35 $\mu C/cm^2$ across a 150 nm thick film). This gave rise to large dielectric permittivity with low loss (ε_r = 775, tan δ < 0.05), negligible temperature-dependence (13% deviation over 500°C) and high-dielectric tunability (greater than 70% across a 300°C range).

4) ***Developing precise control and understanding of ferroic materials: Chemistry and defect control*** – We have regularly used defects and chemistry to effect deterministic change on materials. For example, we used defect dipoles to expand the lattice and increase the transition temperature of $BaTiO_3$, have tweaked chemistry in materials like $BiFeO_3$ and others to tune properties, have used ion beams to effect changes in defect structures in materials like $PbTiO_3$, $BiFeO_3$, and others, induced ferroelectric order in antiferroelectric using cation chemistry, and even tuned local switching behavior in materials by tuning defect structures using a He-ion microscope.

Training Opportunities - Describe opportunities for training and professional development provided to anyone who worked on the project or anyone who was involved in the activities supported by the project. "Training" activities are those in which individuals with advanced professional skills and experience assist others in attaining greater proficiency. Training activities may include, for example, courses or one-on-one work with a mentor. "Professional development" activities result in increased knowledge or skill in one's area of expertise and may include workshops, conferences, seminars, study groups, and individual study. Include participation in conferences, workshops, and seminars not listed under major activities.

The training and professional development activities presented as part of this project include:

1) For the graduate students and postdocs working on the program, extensive one-on-one work with the PI has occurred. In the Martin group, the researchers working on this ARO-supported program took part in weekly sub-group meetings (including the PI) working on related materials and problems. At these meetings the researchers presented their work, discussed challenges and prospects for their research program, and generally interacted at a high level. Additional individual meetings were scheduled to address specific research results and work. The PI works closely with the students on the paper writing process as well – including hands-on, one-on-one sessions working through the text of the papers. The formal meetings were augmented by frequent visits by the PI and discussions of ongoing research in the laboratory on a day-to-day basis.
2) For the undergraduate students working on this program in the Martin group, there were formal weekly meetings (plus informal shadowing and interactions) with the program supported graduate student mentor. In addition to this, the undergraduate student was a participant in the weekly sub-team meetings, and had monthly meetings with the PI and the graduate student mentor to assess progress, understanding of topics, and near- and long-term research and education goals.
3) All graduate students and postdocs supported by this program were participants in regular seminar/presentation training.
4) These experiences were further augmented by weekly group meeting presentations hosted by the PI. The PI supervises a graduate student organized formal research symposium for their group members at which the weekly presenter gives a lengthy and detailed presentation and is subject to ample questions advice. This is one of the most well-received professional development activities and really forces students to up their game.
5) The graduate students and postdocs supported on this program gave oral and poster presentations on their research at various national meetings, including different MRS, EMA, APS, etc. meetings.
6) The graduate students and postdocs supported by this program have participated in the writing of successful user proposals to the CNMS at Oak Ridge National Laboratory and APS at Argonne

National Laboratory and have spent multiple batches of time at both institution completing program-related work.

Results Dissemination - Describe how the results have been disseminated to communities of interest. Include any outreach activities that have been undertaken to reach members of communities who are not usually aware of these research activities, for the purpose of enhancing public understanding and increasing interest in learning and careers in science, technology, and the humanities.

The results of this work have been disseminated to the communities of interest in multiple ways:

1) The supported students, postdocs, and PI have generated publications – 70 of which have been published during the duration of this work – which have and, will continue, to be disseminated in high-impact, peer-reviewed journals that are read by the community.
2) The students, postdocs, and PI are presenting presentations and posters at national conferences and workshops attended by members of the research community. This includes invited talks for the PI at meetings around the world.
3) The PI participates in considerable outreach to prospective undergraduate scientists and engineers and includes in presentations and demonstrations presented to this students aspects of research that are derived from this program. These sessions often include family members (parents, siblings) and thus the message reaches a wide-range of people. PI Martin has also spoken, on the record, at numerous public panels aimed at educating the general public about the needs for and importance of sustained, long-term support of basic research initiatives.
4) PI Martin is actively participating as a scientific adviser for a start-up company and is applying the know-how derived in part from this ARO-supported program to the development of new high-tech industries in the United States.

Honors and Awards

1. 2018, 2019 Highly Cited Researcher – Ranked in the top 1% by citations for field and publication year in Web of Science (Nov. 2018, 2019)
2. 2019 Zeiss ORION NanoFab Prize, Carl Zeiss SMT, Inc. (for innovative work on using ion beams to control material properties and the demonstration of the value of the NanoFab) (Oct. 2019).
3. IEEE-Ultrasonics, Ferroelectrics, and Frequency Control (UFFC) Society Ferroelectrics Young Investigator Award (July 2019)
4. Defense Science Study Group (DSSG) 2020-2021, Institute for Defense Analyses (IDA) and Defense Advanced Research Projects Agency (DARPA) (Mar. 2019)
5. 2017 Excellence in Laboratory Safety Grand Prize, UC Berkeley Environmental, Health, and Safety (EHS) (Feb. 2018)
6. Robert L. Coble Award for Young Scholars, American Ceramic Society (Oct. 2016)
7. American Association for Crystal Growth (AACG) Young Author Award (Aug. 2015)

Tech Transfer

The team continues interactions to support technology transfer, including:

1) Increased and Sustained Interactions with the Army Research Laboratory (Adelphi, MD) – Building from a number of years of continued interactions with Dr. Ron Polcawich and Dr. Brendan Hanrahan at ARL, strong relationships are now being formalized with Cooperative Agreements and co-funding opportunities. PI Martin has visited Dr. Ron Polcawich (now on rotation at DARPA), Dr. Brendan Hanrahan, Mr. Jeff Pulskamp, Dr. Ryan Rudy, Dr. William Nothwang, and others, to lay the foundation for the Cooperative Agreement – a small version of which is now in place. Based on the efforts of PI Martin and others, there are numerous funding avenues for joint efforts to explore the translation and scaling of materials systems developed by PI Martin to ARL efforts. In particular, efforts in high-frequency/microwave dielectrics, advanced actuator, and pyroelectric energy conversion – leveraging

the efforts and materials developed in this ARO program – are planned. Materials are being exchanged. This work is a highly complimentary application to the core programmatic goals of this ARO program.

2) Interactions with Neothermal Energy Company (Atlanta, GA) - Continued interactions as a Scientific Advisor for this small start-up company working on the commericalization of pyroelectric energy conversion for waste-heat energy conversion. Commensurate with the work with ARL, this work is highly complimentary application to the core programmatic goals of this ARO program.

Products

No-Cost Extension

1) A. Fernandez, J. Kim, D. Meyers, **L. W. Martin**, Finite-size effects in lead scandium tantalate relaxor thin films. *Phys. Rev. B* **101**, 094102 (2020). [Editor's Suggestion] [DOI: 10.1103/PhysRevB.101.094102]
2) E. Lupi, A. Ghosh, S. Saremi, S. Pandya, G. Velarde, A. Fernandez, **L. W. Martin**, Large polarization and susceptibilities in artificial morphotropic phase boundary $PbZr_{1-x}Ti_xO_3$ superlattices. *Adv. Electron. Mater.* 1901395 (2020). [DOI: 10.1002/aelm.201901395]
3) H. Taz, B. Prasad, Y.-L. Huang, Z. Chen, S.-L. Hsu, R. Xu, V. Thakare, T. S. Sakthivel, C. Liu, M. Hettick, R. Mukherjee, S. Seal, **L. W. Martin**, A. Javey, G. Duscher, R. Ramesh, R. Kalyanaraman, Integration of amorphous ferromagnetic oxides with multiferroic materials for room-temperature magnetoelectric spintronics. *Sci. Rep.* **10**, 3583 (2020). [DOI: 10.1038/s41598-020-58592-5]
4) B. Guzelturk, A. B. Mei, L. Zhang, L. Tan, P. Donahue, A. G. Singh, D. G. Schlom, **L. W. Martin**, A. M. Lindenberg, Light-induced currents at domain walls in multiferroic $BiFeO_3$. *Nano Lett.* **20**, 145-151 (2020). [DOI: 10.1021/acs.nanolett.9b03484]
5) R. Gao, S. Pandya, Y. Dong, H. Zhao, A. I. Luo, L. R. Dedon, V. Thoreton, R. Xu, S. Saremi, T. Chen, A. Jain, T. Ishihara, D. R. Trinkle, N. H. Perry, **L. W. Martin**, Designing optimal perovskite structure for high ionic conduction. *Adv. Mater.* **32**, 1905178 (2020). [DOI: 10.1002/adma.201905178]
6) L. Zhang, Y.-L. Huang, G. Velarde, A. Ghosh, S. Pandya, D. Garcia, R. Ramesh, **L. W. Martin**, Enhanced pyroelectric properties of $Bi_{1-x}La_xFeO_3$ thin films. *APL Mater.* **7**, 111111 (2019). [DOI: 10.1063/1.5128413]
7) S. Saremi, J. Kim, A. Ghosh, **L. W. Martin**, Defect-induced (dis)order in relaxor ferroelectric thin films. *Phys. Rev. Lett.* **123**, 207602 (2019). [DOI: 10.1103/PhysRevLett.123.207602]
8) S. Chen, H. Zhou, X. Ye, Z. Chen, J. Zhao, S. Das, C. Klewe, L. Zhang, E. Lupi, P. Shafer, E. Arenholz, D. Jin, H. Huang, Y. Lu, X. Li, M. Wu, S. Ke, H. Xu, X. Zeng, C. Huang, **L. W. Martin**, L. Chen, Versatile and highly efficient controls of reversible topotactic metal-insulator transitions through proton intercalation. *Adv. Funct. Mater.* 1907072 (2019). [DOI: 10.1002/adfm.201907072]
9) J. C. Agar, B. Naul, S. Pandya, S. van der Walt, J. Maher, R. Yao, T. Smidt, J. B. Neaton, Sergei V. Kalinin, R. K. Vasudevan, Y. Cao, J. S. Bloom, **L. W. Martin**, Revealing ferroelectric switching character using deep recurrent neural networks. *Nature Commun.* **10**, 4809 (2019). [DOI: 10.1038/s41467-12750-0]
10) G. Velarde, S. Pandya, L. Zhang, D. Garcia, E. Lupi, R. Gao, J. Wilbur, C. Dames, **L. W. Martin**, Quantifying intrinsic, extrinsic, dielectric, and secondary pyroelectric responses in $PbZr_{1-x}Ti_xO_3$ thin films. *ACS Appl. Mater. Inter.* **11**, 35146-35154 (2019). [DOI: 10.1021/acsami.9b12191]
11) X. Lu, Z. Chen, Y. Cao, Y. Tang, R. Xu, S. Saremi, Z. Zhang, Y. Dong, S. Das, H. Zhang, L. Zheng, W. Lu, J. Li, L. Chen, H. Li, W. Cao, **L. W. Martin**, Non-local domain switching in ferroelectric thin films. *Nature Commun*. **10**, 3951 (2019). [DOI: 10.1038/s41467-019-11825-2]